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Supporting Information

Rotational Reorganization of Doped Cholesteric Liquid Crystalline Films

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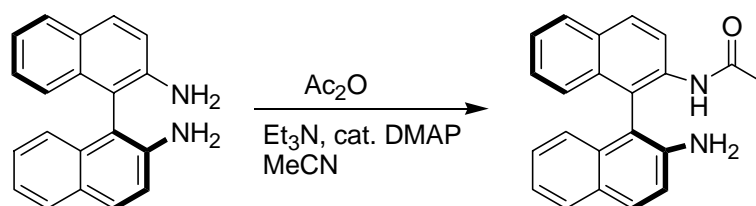
Materials

All solvents were HPLC or spectroscopic grade, and were used as received. All chemicals were obtained from Aldrich, Acros, Merck or Fluka, and were used as received. The liquid crystalline

material E7 was purchased from Merck, Darmstadt.¹ The liquid crystalline material MLC-6815 was received as a gift from Merck, Darmstadt. Its average molecular weight is 288.38 g/mol. Glycine, NaCl and Na₂SO₄ were technical grade, and ground to a fine powder in a mortar prior to use. Glass rods were obtained from the Department of Polymer Technology, Eindhoven University of Technology, for which they are gratefully acknowledged. The synthesis and characterization of molecular motors **1-4** was previously described.² The absolute configurations of molecular motors (2'*S*)-(P)-**1**, (2'*S*)-(M)-**2**, (2'*S*)-(P)-**3** and (2'*R*)-(P)-**4** were determined by comparison of their circular dichroism (CD) spectra to the CD spectra of a similar motor of known configuration.³ Chiral dopant (*S*)-**S1** was prepared according to a literature procedure.⁴

Synthesis of azobenzene switch (S)-5

Azobenzene switch **5** was synthesized according to a literature procedure⁵, with a modification of the synthetic procedure of the first step. Apart from the first step, yields and spectral data were in accordance with literature values.⁵ In the first step, the mono-acetylation of (*S*)-2,2'-diamino-1,1'-binaphthyl was accomplished using the following procedure.



Acetic anhydride (0.31 ml, 3.3 mmol) in acetonitrile (10 ml) was added dropwise to a solution of (*S*)-2,2'-diamino-1,1'-binaphthyl (720 mg, 2.53 mmol) and Et₃N (0.46 ml, 3.3 mmol) in acetonitrile (30 ml) at 0 °C. A catalytic amount of DMAP was added and the reaction mixture was allowed to warm to room temperature overnight. Methanol (1 ml) was added and the reaction mixture was stirred for an additional 15 min. A saturated aqueous solution of NH₄Cl was added and the acetonitrile was removed using the rotary evaporator. The residue was extracted twice with CH₂Cl₂; the organics were washed with water and dried with Na₂SO₄. The crude product contained a 1:1 mixture of mono- and diacetylated product.

The desired mono-acetylated product was isolated by column chromatography (SiO₂, pentane : EtOAc = 1:1 → 1:2 gradient) in 40% yield (330 mg, 1.0 mmol). Spectral data were identical to literature values.⁵

Equipment

Microscope

Images and movies of the moving particles were recorded in transmission using an Olympus BX 60 microscope, equipped with polarizers and a Sony 3CCD DXC 950P digital camera, attached to a personal computer with Matrox Inspector 2.1 imaging software.

Lamp

For irradiation a Spectroline model ENB-280C/FE lamp was used at $\lambda = 365 \text{ nm}, \pm 5 \text{ nm}$. The lamp was held at an angle of 45° with respect to the sample plane, to allow irradiation under the microscope. The distance between the lamp and the sample was approximately 15 cm.

Preparation of liquid crystalline films

A microscope slide was thoroughly cleaned, spin-coated with a commercially available polyimide (Optmer AL1051, JSR, Belgium) and allowed to harden overnight in a vacuum oven (170 °C, 200 mbar). The surface was then rubbed with a polyester fabric to induce parallel alignment in the liquid crystalline samples. A toluene solution of the liquid crystal and chiral dopant was then deposited on this surface and the toluene was allowed to evaporate to give a cholesteric liquid crystalline (LC) phase of a few microns. After multiple sample preparations, we observed that exact film thickness was not a determining parameter in the properties of the system.

The viscosity of the liquid crystals (typically $\text{Viscosity}_{20^\circ\text{C}} = 27 \text{ mm}^2/\text{s}$ for MLC-6815) is drastically modified by introduction of chiral dopants. Therefore, viscosities are not reported here. The transition temperatures of the LCs used are as follows:

E7	$T_m = -10\text{ }^{\circ}\text{C}$	$T_c = 60\text{ }^{\circ}\text{C}$
K15	$T_m = 24\text{ }^{\circ}\text{C}$	$T_c = 35\text{ }^{\circ}\text{C}$
pCH5	$T_m = 29.7\text{ }^{\circ}\text{C}$	$T_c = 55.0\text{ }^{\circ}\text{C}$
MLC-6815	$T_m < 20\text{ }^{\circ}\text{C}$	$T_c = 67.0\text{ }^{\circ}\text{C}$
MBBA	$T_m = 21\text{ }^{\circ}\text{C}$	$T_c = 47\text{ }^{\circ}\text{C}$

General procedure for determination of the cholesteric pitch

The pitch of the liquid crystalline phases was determined by Grandjean-Cano technique,⁶ using plane-convex lenses of known radii ($R = 25.119$ or 30.287 mm, Linos Components; Radiometer), and an Olympus BX 60 microscope. Using stock solutions of E7 and the chiral dopant in toluene, mixtures of these two compounds were made. The concentration of the chiral dopant in E7 was normally between 0.5 and 1.5% wt/wt. This solution was applied on a linearly rubbed, polyimide-coated surface (vide supra) and after the toluene had evaporated in the air, the glass plate was put under the microscope. After applying a plane-convex lens of known diameter, Grandjean-Cano lines could be observed which allowed the determination of the cholesteric pitch by measuring the distances between the consecutive lines. The sign of the helical pitch was determined with a contact method.⁷ Mixed samples with a doped cholesteric liquid crystal of known negative screw sense were used, consisting of dopant ZLI-811 (Merck, Darmstadt, Germany) in E7. Reported helical twisting powers are determined in mol dopant per mol LC, assuming an average molecular weight of 271.2 g/mol for E7.

Particle rotation

All particles were placed on the LC film by sprinkling them on a freshly prepared LC film. Using the optical microscope their rotation could be observed during irradiation and thermal steps. The glass rods (diameter 3.2, 5.0 and 10.0 μm) were obtained from Merck as a gift.

Control experiments regarding the rotational reorganization of LC films

As a control experiment a cholesteric LC film with a polygonal texture was generated using a photoinactive chiral dopant (binaphthalene (*S*)-**S1**).⁸ Irradiation of this film with 365 or 430 nm light did not lead to any observable change of the texture (Figure S1). This confirms that the rotational reorganization is directly connected to a photochemical (and thermal) process at the level of the molecular motor.

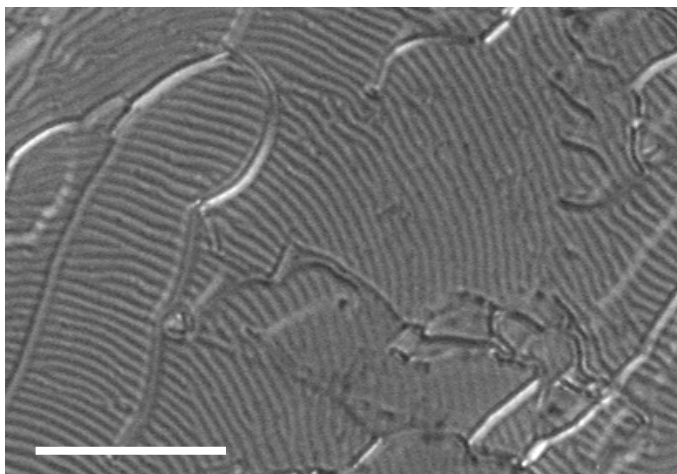
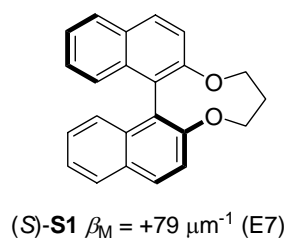


Figure S1 An optical micrograph of E7 doped with binaphthalene (*S*)-**S1** (1.6 wt%). Irradiation with 365 nm light had no visible influence on the appearance of this texture. Scalebar, 50 μm .

Depending on the dopant and the LC host, the helical twisting power of a dopant can change in response to heating or cooling the system.⁹ To ensure that the observed changes in helical twisting power were not caused by simple heating of the sample by the UV lamp, an LC film consisting of E7 doped with 1 wt% (*P*)-**1** was heated up to the N*-I phase transition point, while kept in the dark. At various temperatures the helical twisting power was measured, the results of which are shown in Figure S2.

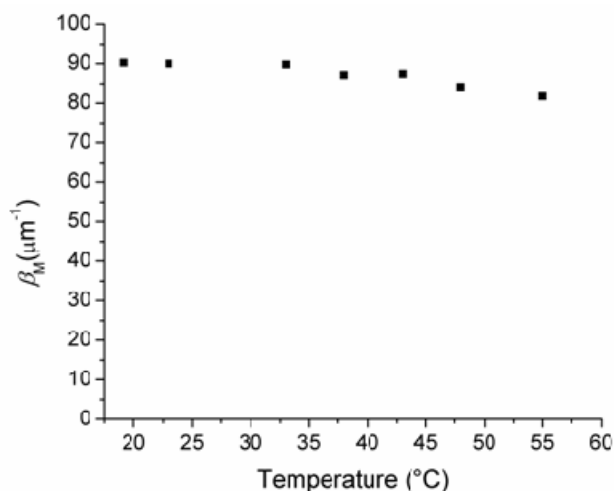


Figure S2 The helical twisting power (β_M) of 1 wt% (*P*)-**1** in E7 as a function of temperature. The LC film melted at 57°C.

The N*-I phase transition was observed at 57°C. Before that point the helical twisting power of (*P*)-**1** changed by only 10%, which confirms that the observed changes in helical twisting power upon irradiation with UV light are the result of the photochemical isomerization of the central alkene of the motor.

Atomic force microscopy

AFM measurements were performed at room temperature and under ambient conditions on a Nanoscope IV (Digital Instruments, Santa Barbara, CA) at the Department of Physics of the University of Groningen. In all experiments heavily doped commercially available silicon cantilevers with a resonance frequency of ~300 kHz were used for imaging in non-contact mode. Experiments were performed in several sessions using different tips to check for reproducibility and to avoid artifacts.

Automated picture processing

The angular displacement of a glass rod and the rotational reorganization of an arbitrarily chosen section of polygonal texture next to it were recorded during irradiation and thermal step. These rotations were digitized by an octave routine (the software is available free of charge at www.octave.org).

Digitizing of the rotation of a given area of the LC texture was achieved by applying the following steps. After selecting a square area of $28.8 \times 28.8 \mu\text{m}^2$ located at an approximate distance of $40 \mu\text{m}$ on the right of the glass rod (see Fig. S3a), the brighter points of the picture were selected. Among those, only the points surrounded by other bright points were considered (see Fig. S3b) and eventually the representative worm-like feature selected was the biggest component of connected bright points, i.e. the biggest aggregation of pixels marked in red (see Fig. S3c). Calculating the coordinates of the bright points belonging to this biggest connected component allowed the determination of the angle of that feature with respect to a fixed arbitrary direction.

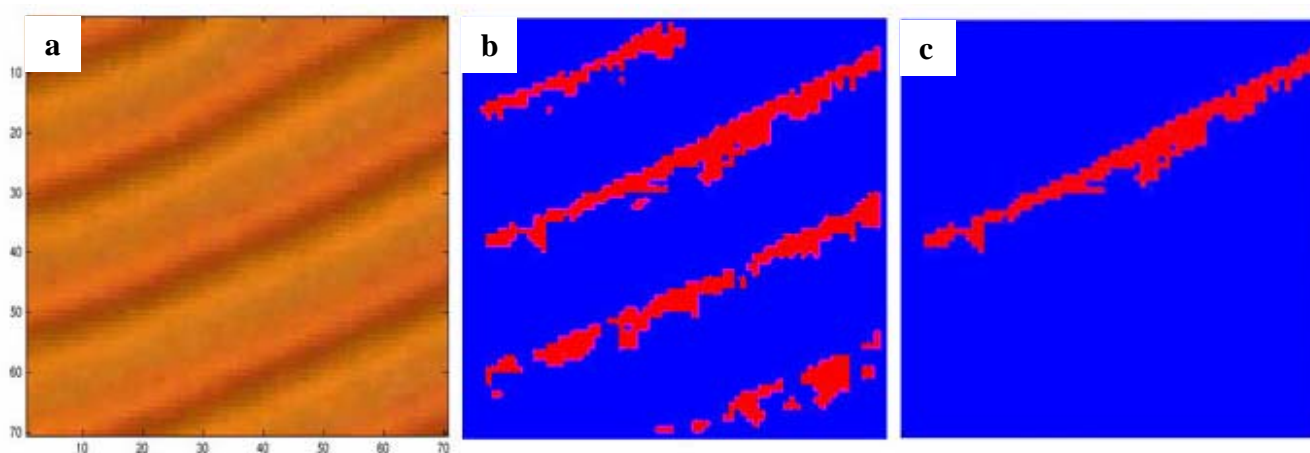


Figure S3 Representative steps of the picture processing applied for digitalizing the rotation of the LC texture. (a) The window chosen is a square area of 70×70 pixels corresponding to a real area of $28.8 \mu\text{m} \times 28.8 \mu\text{m}$ (b) Applying a threshold allows the extraction of characteristic features of the texture, depicted in red. (c) The biggest set of connecting points is finally selected as the representative feature of the area. In this example the determined orientation of the texture is 0.57 rad with respect to the horizontal.

Digitization of the rotation of the glass rod was achieved by applying the following treatments to the raw data. A rectangular area of approximately $80 \mu\text{m} \times 40 \mu\text{m}$ was selected with the glass rod in its center. For some pictures the center of this window was shifted in such a way that the glass rod always remained roughly in the center. Similarly than in the routine used for the texture, a threshold was applied in order to select only the brighter points of this window. Then, because of the irregular borders

of the rod, an outline detection was carried out with help of a Laplacian filter. The angle of the obtained feature was finally determined with respect to an arbitrary chosen, fixed direction.

For comparison of the displacement of the rod and the texture, their respective ratios were determined during both irradiation and thermal steps. In both cases, the first datapoint obtained for the rotation of the texture was arbitrarily assigned as $t = 0$ s and $\theta = 0$ rad. The ratios are shown in Figure S4.

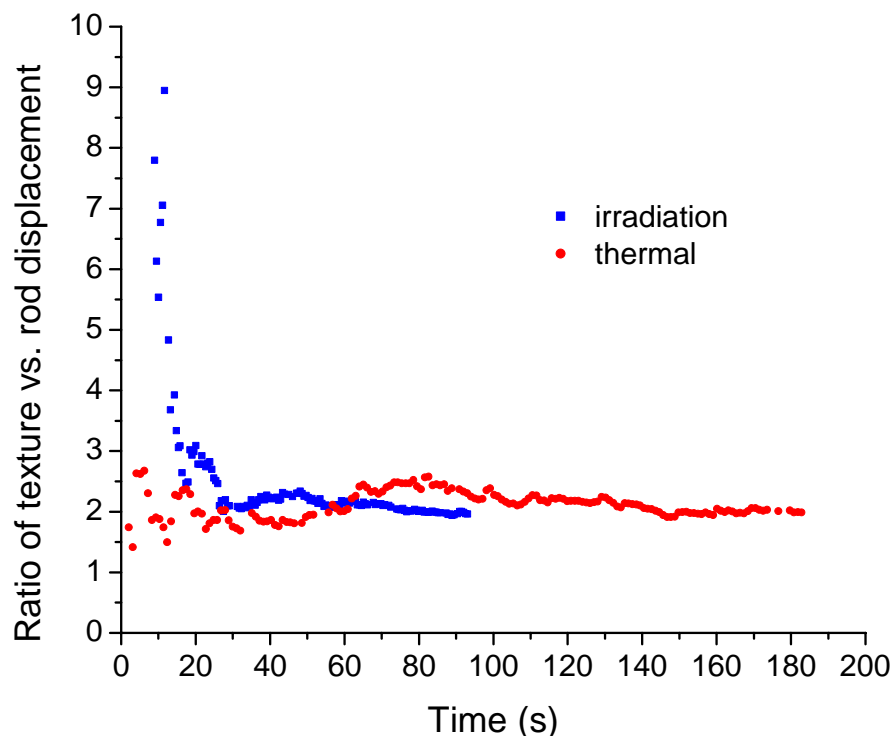


Figure S4 Ratio of texture vs. rod displacement over time, during irradiation (blue squares) and thermal (red dots) step of the rotational process. The data used is shown in Figure 7.

Determination of work performed

The calculations of work were performed on the system using a glass cyclinder which was $28 \mu\text{m}$ long as determined by optical microscopy. Thus, given an average value for density of bulk glass ($\rho = 2.5 \times 10^3 \text{ kg/m}^3$),¹⁰ it has a mass of $(1.4 \pm 0.1) \text{ ng}$. The moment of inertia (I) was determined using $I = 1/4MR^2 + 1/12ML^2$.^(ref 11) The initial angular acceleration of the rod during the photochemical step of the

described process was determined by second order polynomial fit to the angular displacement in the first 20 seconds. The fit showed a linear acceleration (α) of 0.0068 rad/s^2 . Assuming a moment of inertia (I) of $9.19 \cdot 10^{-23} \text{ kgm}^2$ for this particular glass rod, a constant torque (τ) of $6.25 \cdot 10^{-25} \text{ Nm}$ is obtained.¹¹ Consequently, when the rod makes one full rotation, $3.93 \cdot 10^{-24} \text{ J}$ of work is done.

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⁸ Dopant (*S*)-**S1** is photoinactive at these wavelengths, however, at lower wavelengths an inefficient photoracemization can occur ($\lambda < 330 \text{ nm}$). See Zhang, M.; Schuster, G. B. *J. Phys. Chem.* **1992**, *96*, 3063-3067.

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